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REGULAR ARTICLE

Isoprene and α-pinene deposition to grassland mesocosms

Felix M. Spielmann · Stephan Langebner · Andrea Ghirardo · Armin Hansel · Jörg-Peter Schnitzler · Georg Wohlfahrt

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Abstract
Background and aims Isoprene and monoterpenes account for approximately two thirds of the biogenic volatile organic compounds (BVOC) emitted annually by vegetation into the atmosphere. Previous research focussed on the magnitude of and controls on emissions of these two compounds by emitting plant species, while the role of soils and non-emitting plant species as potential sinks has been mostly ignored. The objective of the present study is to characterize the deposition of isoprene and α-pinene (a monoterpene) to non-emitting grassland plant mesocosms.
Methods We conducted a laboratory experiment with mesocosms of two forb and one graminoid plant species. Plants and soils together and bare soils only were subject to increasing ambient isoprene and α-pinene concentrations (0–10 ppbv) and the corresponding BVOC exchange rates were quantified.
Results Our major findings are that (i) soils were the dominant sink for the deposition of α-pinene and isoprene in grassland mesocosms, (ii) the presence of above-ground biomass of non-emitting plant species decreased the isoprene and α-pinene deposition in the majority of all cases, and (iii) the net deposition correlated inversely with the ambient concentrations.
Conclusions Our results call for a more in-depth analysis of soil BVOC exchange to better estimate the contribution of soils to the ecosystem-atmosphere BVOC exchange.

Keywords BVOC · Soil · Deposition · Isoprene · Monoterpenes

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F. M. Spielmann · G. Wohlfahrt (✉)
Institut für Ökologie, Universität Innsbruck, Sternwartestr. 15, 6020 Innsbruck, Austria
e-mail: georg.wohlfahrt@uibk.ac.at

S. Langebner · A. Hansel
Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, 6020 Innsbruck, Austria

A. Ghirardo · J.-P. Schnitzler
Research Unit Environmental Simulation (EUS), Institute of Biochemical Plant Pathology, Helmholtz Zentrum München GmbH, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany

G. Wohlfahrt
Europäische Akademie Bozen, Drususallee 1, 39100 Bozen, Italy

Introduction

The biosphere, and in particular higher plants, annually emit approximately 1000 Tg of carbon as volatile organic compounds (VOCs) into the atmosphere (Guenther et al. 2012). These biogenic VOCs (BVOCs), i.e. isoprene and monoterpenes, play a significant role in global atmospheric chemistry as they affect the atmosphere's oxidising capacity (and thus the life time of other trace gases) and may react to form secondary organic aerosols and cloud condensation nuclei, which modify the planetary albedo and precipitation rates (Arneth et al. 2010; Carslaw

et al. 2010; Claeys et al. 2004; Kulmala et al. 2004; Paulot et al. 2009).

Recently it became clear that in addition to the chemical atmospheric sink, dry deposition of BVOCs to vegetation might be playing a more significant role than previously thought (Bamberger et al. 2011; Karl et al. 2005; Karl et al. 2004; Laffineur et al. 2012; Park et al. 2013). Corresponding empirical data, however, are still scarce and the mechanisms of VOC deposition to ecosystems (relative roles of deposition to the soil or plant surfaces and stomatal uptake) are poorly understood and thus crudely represented in atmospheric chemistry models (Galbally and Kirstine 2002; Guenther et al. 2012; Millet et al. 2008).

Isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) together are thought to contribute more than 69 % of the total BVOCs annually emitted to the atmosphere (Guenther et al. 2012). In contrast to other BVOCs, which are emitted by all plants (e.g. methanol and acetaldehyde) (Fall and Benson 1996), isoprene and monoterpene emission is plant species- and partly family-specific (Benjamin et al. 1996; Csiky and Seufert 1999; Karlik and Winer 2001; Klinger et al. 1998). For ecosystems such as coniferous or oak-dominated deciduous forests, consisting of strong isoprene and/or monoterpene emitting plant species (Laffineur et al. 2013), deposition of these compounds, compared to their emission, is often minor (Karl et al. 2004). In contrast, deposition of isoprene and monoterpenes has been shown to be significant in case of ecosystems whose plant species are no or very weak emitters of these volatile isoprenoids. For example, Bamberger et al. (2011) showed that a mountain grassland ecosystem (dominated by grass, clover and buttercub species) turned into a significant sink for monoterpenes during an extended period of elevated (up to 7.5 ppbv) ambient monoterpene concentrations. The monoterpene-enriched air masses were advected to the grassland from the surrounding coniferous forest, which emitted high amounts of stored monoterpenes due to mechanical damage after a hail storm. Before the hailstorm, when monoterpene ambient concentrations were below 1 ppbv, the grassland was neither a sink nor a source for monoterpenes. Similarly, Aaltonen et al. (2012) observed monoterpene deposition to non-emitting understory plant species advected from neighbouring emitting plant species in a coniferous forest.

As the exchange of BVOCs between an ecosystem and the atmosphere results from the corresponding partial pressure gradient times a (combined turbulent and diffusive) transfer velocity, the deposition of BVOCs will be observed whenever the ambient partial air pressure exceeds the ecosystem-internal one. For ecosystems dominated by emitting plant species, internal BVOC partial pressures are typically high enough (Fall and Monson 1992; Niinemets and Reichstein 2003) that deposition will occur only during periods of exceptionally high ambient concentrations. For ecosystems composed mainly by non-emitting plant species, in contrast, deposition may be more ubiquitous, as internal partial pressures are likely to be very low. A recent study also showed that reactions with semi-volatile organic compounds, emitted from plant surfaces may act as a sink for ozone. This could hint to an additional mechanism to loss of other reactive compounds at plant or soil surfaces (Jud et al. 2015).

The objective of the present study is to characterize the deposition of isoprene and α-pinene (a monoterpene) to non-emitting typical mountain grassland plant species occurring at the field site of Bamberger et al. (2011). Therefore we conducted a laboratory experiment with mesocosms of two forb and one graminoid plant species derived from this grassland. These mesocoms, i.e. plants and soils together and bare soils, were subject to increasing ambient isoprene and α-pinene concentrations (0–10 ppbv) and the corresponding BVOC (plus CO_2 and H_2O) exchange rates were quantified.

With this work we aim testing two hypotheses (H): (i) The isoprene and α-pinene exchange of the investigated non-emitting plant species and soil mesocosms scales negatively with the corresponding ambient concentrations due to an increase in the diffusion gradient (H1). (ii) Mesocosms including above-ground vegetation exhibit higher net emission/lower net deposition compared to soils alone, due to residual emissions of isoprene and α-pinene by the above-ground plant parts (H2).

Material and methods

Plants and soil

Three plant species, *Trifolium pratense*, *Dactylis glomerata* and *Ranunculus acris* were chosen to represent a legume, a grass and a forb plant species, respectively. All plant species occurred in the mountain grassland study by Bamberger et al. (2011), during which a

prolonged period of monoterpene deposition was observed to a grassland ecosystem associated with elevated ambient isoprenoid concentrations. The vegetation of this grassland ecosystem consisted of about 28 % grasses, 11 % *Trifolium pratense* and *Trifolium repens* and 4 % *Ranunculus acris*.

The plants for our experiment were grown for three months from seeds in pots with a surface area of 64 cm^2 inside a greenhouse in Innsbruck, Austria. The soil consisted of steamed (for sterilisation) leaf mold, steamed basic soil, lava, coconut fibre, sand and rock flour (31 %, 15 %, 12 %, 15 %, 15 % and 12 % respectively), which was used by the Botanical Garden of the University of Innsbruck to simulate the soil of the study site by Bamberger et al. (2011). After their transport to the greenhouse facility of the EUS in Munich, the plants were subject to 14 h of a combination of natural and, when needed, artificial light with a close-to-natural wavelength composition (Powerstar HQI-TS, 400 W/D, OSRAM, Germany) to keep the incoming radiation stable. Day and night temperatures were set constant at 25° and 10 °C, respectively. All experiments were conducted during daytime and started when the photosynthesis and respiration rates of the plants and soils in their chambers were stable.

Experimental setup

For analysis the plants ($n = 4$ per species) were enclosed in PAR-transparent Perspex glass chambers (V = 5 L) (Fig. 1) to measure the bi-directional exchange of the BVOCs of interest (Ghirardo et al. 2012). Two of these chambers were used at a time to maximise the number of replicates during the experiment. Each of the cuvettes was connected via an inlet and an outlet to one infrared gas analyser (IRGA, GFS-3000, SN: KETA0103 and KETA0147, Heinz Walz, Effeltrich, Germany). These and all other connections were done using Teflon® PFA tubing, thermally insulated and heated wherever necessary to avoid condensation.

A constant flow of air containing 10,000 ppmv H_2O and 380 ppmv CO_2 was supplied to the inlet air to keep the rate of evapotranspiration and photosynthesis stable, starting 20–30 min before the first measurement. Two air pumps (Neuberger diaphragm vacuum pump, KNF, Freiburg, Germany), in combination with several overflow vents, were used to keep a steady flow of air (1280 sccm) throughout the cuvette. To minimize background contamination by ambient BVOCs, two-catalysers (Platinum (Pt) - Palladium (Pd), 390 °C; self-build, (Graus et al. 2010)) were used to purify the inlet air of both cuvettes. The ambient BVOC concentrations in the cuvettes (0, 3, 5 and 10 ppbv) were chosen to simulate similar conditions to the study of Bamberger et al. (2011), who measured monoterpene concentrations from below 1 ppbv to up to 7.5 ppbv. A certified gas standard (Apel-Riemer Environmental Inc., USA) containing isoprene as well as α-pinene was used to increase the concentration of both VOCs in the cuvettes simultaneously.

In order to gradually step through ambient concentrations in the cuvettes two mass flow controllers of 20 sccm (EL-FLOW Select Series Mass Flow Controller; BRONKHORST HIGH-TECH B.V., Ruurlo, Netherlands) were used to mix catalysed VOC-free air with the gas standard. The same mixing ratios (0–10 ppbv) were used for calibration with 10,000 ppm H_2O, corresponding to chamber inlet conditions, prior to each measurement cycle. A calibration with 30,000 ppm H_2O, reflecting typical conditions at the outlet of the chamber, was conducted once for each chamber after the experiment. The corresponding calibration factor was within the range of the calibration factors ($n = 24$) determined with 10,000 ppm H_2O (6.9 ± 0.2 for isoprene and 3.4 ± 0.3 for α-pinene). The conversion from ncps (norm counts per second) as measured by the PTR-ToF-MS to the corresponding ambient concentration in ppbv was thus done based on the calibration factor determined prior to each experiment. The limit of detection for isoprene was on average 0.0078× + 0.03 and 0.0067× + 0.0187 for α-pinene, where x denotes the respective ambient concentration (ppbv) of the BVOC of interest.

Mass analysis was done with the original PTR-ToF-MS developed at the University of Innsbruck. Since PTR-ToF-MS is an already well established method, only a brief description of the fundamental operation principles is given here. A detailed description can be found elsewhere (Graus et al. 2010; Jordan et al. 2009).

PTR-ToF is a chemical ionization mass spectrometer developed at the Institute of Ion Physics at the University of Innsbruck. The instrument can be operated real time to record in situ concentrations. With its high mass resolving power up to m/dm = 5000 and a mass accuracy of less than 10 ppm (parts per million), isobars can be distinguished and empirical formulas can be identified (Graus et al. 2010; Jordan et al. 2009). A mass range of 0–300 m/z was recorded in a one second time resolution. The reaction chamber of the PTR-ToF-MS was operated at standard conditions (60 °C, 2.3 mbar,

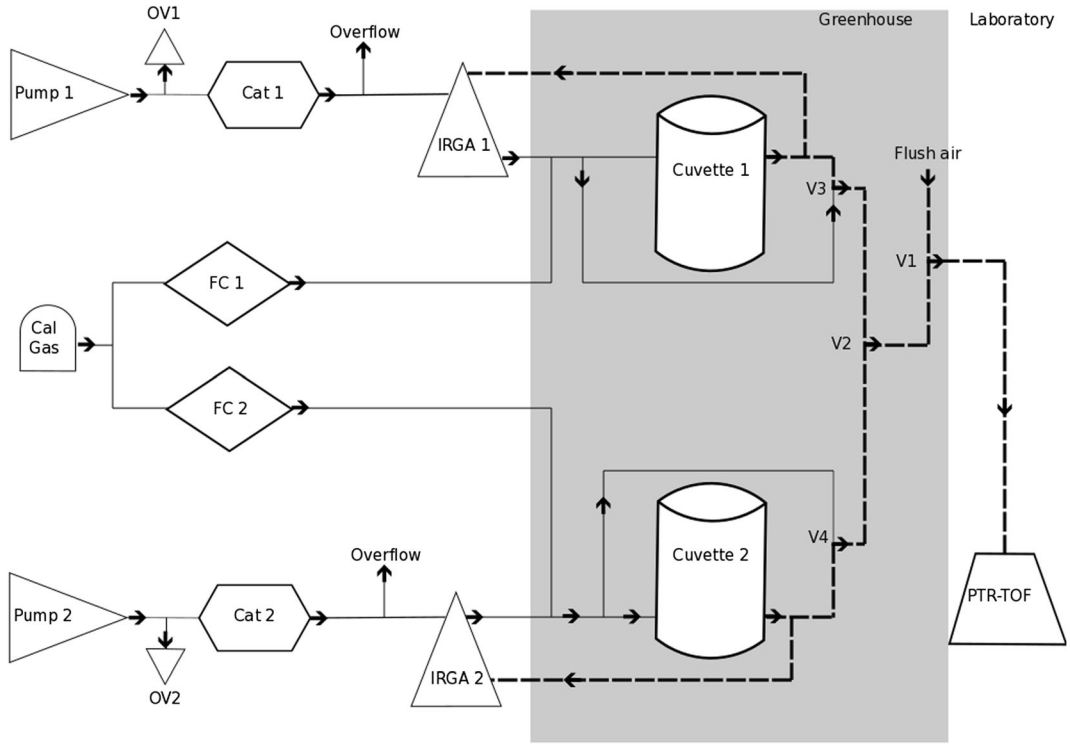

Fig. 1 Schematic drawing of the experimental setup. Pump – vacuum-pump, OV – overpressure valve, cat – catalyser, Overflow – overflow tube, IRGA – infrared gas analyser, Cal Gas – calibration gas cylinder, FC – flow controller, Cuvette – Perspex glass chamber, V – 3-way solenoid valve, Flush air – air intake of PTR-TOF during night time, PTR-TOF – Proton transfer reaction-time of flight mass spectrometer, solid line – non heated Teflon-tube, dashed line – heated Teflon-tube

580 V). For conversion of the raw data to ncps, the "PTR-TOF Data Analyzer" software in version 2.44 was used (Müller et al. 2013; Titzmann et al. 2010).

Four solenoid valves (M Series Miniature Solenoid Valve, Teqcom Industries Inc., Newport, USA) were used to switch the PTR-TOF's connection between inlet and outlet air of the two cuvettes (Fig. 1). A permanent airflow (1280 sccm) was established from and to the IRGAs through the cuvettes to measure the rate of evapotranspiration and photosynthesis continuously. A temperature difference between the cuvettes (29 °C)and the surrounding air (21.5 °C) made it necessary to heat the outlet lines (37 °C/50 °C) to prevent condensation in the tubes (see dashed line in Fig. 1). The temperatures in the cuvettes were measured using two temperature and humidity sensors (Humi-pick: M21816 & M21817, Fa. Spirig, Rapperswil, Switzerland).

In a first measurement cycle (4 h), pots containing soil and above-ground biomass of one of the three plant species mentioned above were placed in the cuvettes, allowed to stabilize the gas exchange, and then exposed to a step-wise increase of VOC-ambient concentration (0,3,5 and 10 ppbv). In order to disentangle the exchange between the bare soil and the above-ground plant biomass, the above-ground parts of the plants were cut after this cycle. After 12 h, the remaining plant material (i.e. main stem) was sealed using a PTFE-paste (to prevent the volatilisation of wounding-induced VOCs (i.e. volatile breakdown products of unsaturated fatty acids: hexenylacetate, Z-hexanol, etc.) as reported by Brilli et al. (2011)). The bare soil was exposed to the same step-wise increase in VOC concentration levels. In between these two principal measurement cycles, which were conducted once per plant and soil, empty cuvettes were measured in the same fashion in order to characterize any residual exchange in the empty cuvettes. These background values were subtracted from the VOC concentrations at the outlet of the cuvettes. Although the inlet VOC concentrations were the same for both pots with vegetation and bare soils, the outlet concentrations differed because of the biological activity inside the cuvettes. Hence the difference between the VOC fluxes from the pots with

vegetation and the soil measurements couldn't be calculated by a simple subtraction and we thus do not explicitly infer the plant contribution by difference, but rather present results separately for pots with bare soils only and pots with vegetation cover and discuss the corresponding differences on a soil surface area basis.

The water vapor, CO_2 and VOC exchanges (E) in the cuvettes were calculated using the formula of Caemmerer and Farquhar (1981).

$$E_x = \frac{(X_o - X_e)f}{A(1-W_o)} \quad (1)$$

Where f represents the flow rate (mol s^{-1}), X_o and X_e the mole fractions (mmol mol^{-1} or μmol mol^{-1} or nmol mol^{-1}) of the air leaving and entering the cuvettes, W_o the water vapor mole fraction (mol mol^{-1}) exiting the cuvette and A represents the exposed soil surface area (0.0064 m^2).

The CO_2 and water vapor exchange was measured to ensure that plants were photosynthetically active and their gas exchange under steady-state conditions. During the experiments, the measured CO_2 mole fraction, air temperature and relative humidity inside the cuvettes did exhibit only slight changes during the course of each measurement cycle (<28 ppm, <5 ° and <23 %, respectively) and was thus regarded as being in steady-state (data not shown). To ensure that no ambient air would enter the cuvettes and tubes, leak-tests were conducted at the beginning of every measurement.

After the gas exchange measurements, the soils were frozen for further analysis at −18 °C. The soil pH was then measured using a pH-meter (Lab pH meter inoLab® pH 110, WTW, Weilheim in Oberbayern, Germany) in a solution of 10 g sieved (2 mm) soil and 25 ml 0.01 M $CaCl_2$. The soils used in this study were slightly acidic with a mean pH of 6.0 ± 0.2.

Statistical analyses

The linear regression model and the statistical group comparison, using a linear regression analysis and a paired t-test, respectively, were conducted using the Matlab statistics toolbox (Matlab Release R2014b, The MathWorks, Inc., Natick, Massachusetts, United States.), after confirming the assumption of normality and heteroscedasticity through QQ-plots and residual plots.

Results

Pots with soils represented a consistent sink for isoprene across all species (Fig. 2). The isoprene flux to bare soils (−0.58 to −0.05 nmol m^{-2} s^{-1}) was significantly ($p < 0.001$) different from the pots including above-ground vegetation (−0.55 to −0.04 nmol m^{-2} s^{-1}). Isoprene deposition did not increase significantly with increasing ambient VOC concentrations both with and without plants being present in the pots ($p > 0.05$; Fig. 2), although a trend to increasing deposition at higher ambient VOC concentrations was visible. A significantly stronger uptake of isoprene at higher ambient VOC concentrations was observed in 3, 4 and 3 including, and in 2, 4 and 2 cases out of 4 replicates excluding above-ground biomass of *Dactylis glomerata*, *Trifolium pratense* and *Ranunculus acris,* respectively. Since no emission values were observed for isoprene, no compensation points could be found for pots containing soils, as well as pots containing soils and above-ground biomass.

Similarly to the gas exchange of isoprene, α-pinene deposition dominated in the pots with bare soils (net deposition in 94 % of all cases across all species; Fig. 3). As for isoprene, monoterpene deposition to soils was also significantly stronger compared to the pots including above-ground vegetation ($p < 0.001$), which were a sink for α-pinene in only 19 % (Fig. 3) of all cases across all species. The deposition of α-pinene to soils was significantly inversely related to ambient concentrations ($p < 0.01$), which was not the case for pots with above-ground vegetation ($p > 0.05$), although again in most cases a trend to lower emission/higher deposition at higher ambient VOC concentrations was visible (Fig. 3). In case of *Dactylis glomerata*, a compensation point was observed for pots including above-ground biomass, net emission/deposition of α-pinene prevailing below/above ambient concentrations of 10.1 ppbv (Fig. 3), which is in the upper range of our measured ambient concentrations. Responsible for the change from emission to deposition is replicate *number 3*, for which a compensation point of 5.7 ppbv was inferred. For replicates number 1 and 2 a decrease in emission with increasing ambient concentration was observed until the flux was below the limit of detection at ambient concentrations of 9.4 and 9.7 ppbv (Fig. 3). Compared to isoprene a significantly stronger uptake of α-pinene at higher ambient VOC concentration was only observed in 0, 0 and 2 including, and in 3, 2 and 3 cases out of 4

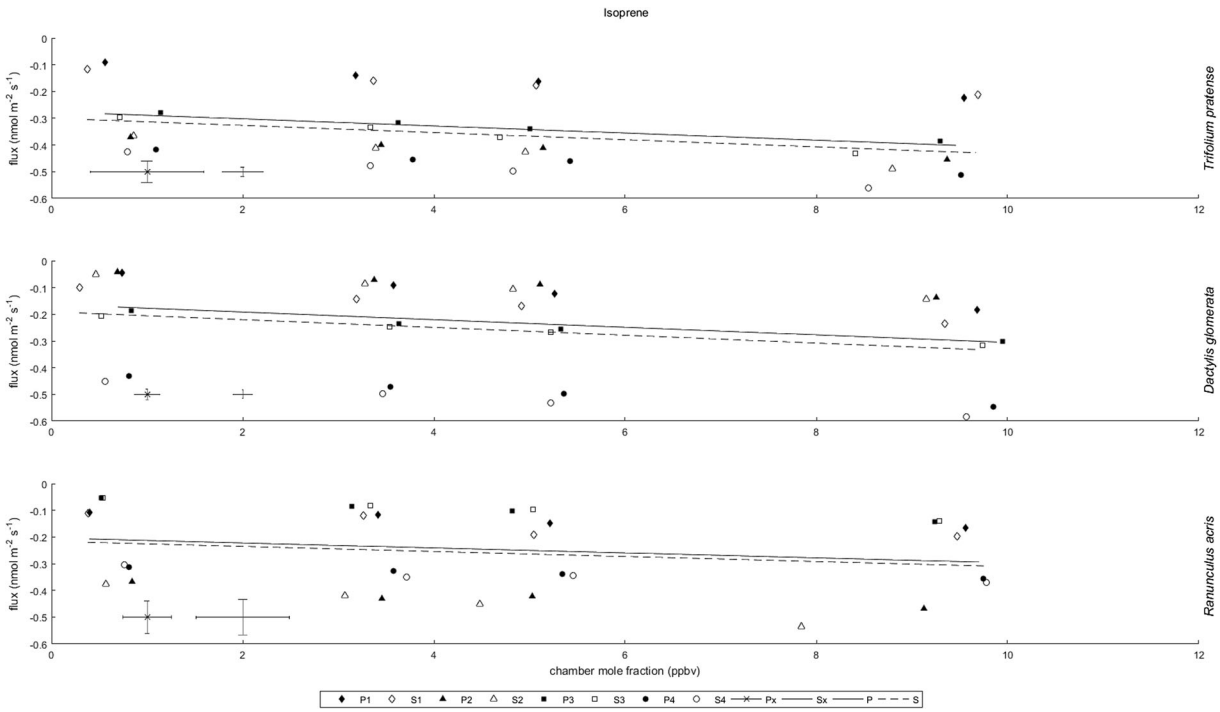

Fig. 2 Isoprene exchange of *Ranunculus acris* (lower panel), *Dactylis glomerata* (middle panel) and *Trifolium pratense* (upper panel) as a function of the ambient isoprene mole fraction. Negative fluxes denote deposition. Open symbols and dashed lines indicate pots with bare soils (S), while closed symbols and solid lines indicate pots with above-ground plant biomass (P) being present. For each plant species four replicate pots were investigated (n = 4). Each data point represents the average of 15 min of measurements at the same ambient mole fraction; the maximum standard deviations per measurement cycle (over the course of all BVOC ambient concentrations) are indicated in the lower left corner of each panel. Grey symbols indicate fluxes below the limit of detection, which were excluded from the statistical analysis

replicates excluding above-ground biomass of *Dactylis glomerata*, *Trifolium pratense* and *Ranunculus acris,* respectively.

For both isoprene and α-pinene slopes of exchange rates vs. ambient concentrations did not differ significantly ($p > 0.05$) between pots with and without above-ground vegetation (Figs. 2 and 3).

Discussion

The objective of the present study was to investigate the deposition of isoprene and α-pinene to typical non-emitting mountain grassland mescocosms. A laboratory experiment with mesocosms of three different grassland plant species, which were subject to increasing ambient isoprene and α-pinene concentrations, was conducted and the corresponding VOC exchange rates were quantified.

Our first hypothesis (H1) aimed at testing whether the isoprene and α-pinene exchange scales negatively with the corresponding ambient concentrations. The main idea underlying this hypothesis is that by increasing ambient concentrations the gradient to the interior of the investigated non-emitting plant species (with intercellular partial pressures presumably close to zero) and soils would be increased, resulting in a larger deposition. While slopes of linear regressions between ambient isoprene and α-pinene concentrations and the respective exchange rates were negative (Figs. 2 and 3), the corresponding slope including all soils was significantly different from zero only for α-pinene, but only for 8 out of 12 pots containing soils across all species, for isoprene. We thus have to partially reject hypothesis H1.

The ability of soils to deposit isoprene has been demonstrated in several studies. Cleveland and Yavitt (1997) and Pegoraro et al. (2006) suggested a biologically-mediated isoprene uptake by soil microorganisms. The ambient concentrations in the studies of Cleveland and Yavitt (1997) and Pegoraro et al. (2006) ranged from 508 ppbv to 200–1200 ppb, respectively, and were thus up to one order of magnitude higher in

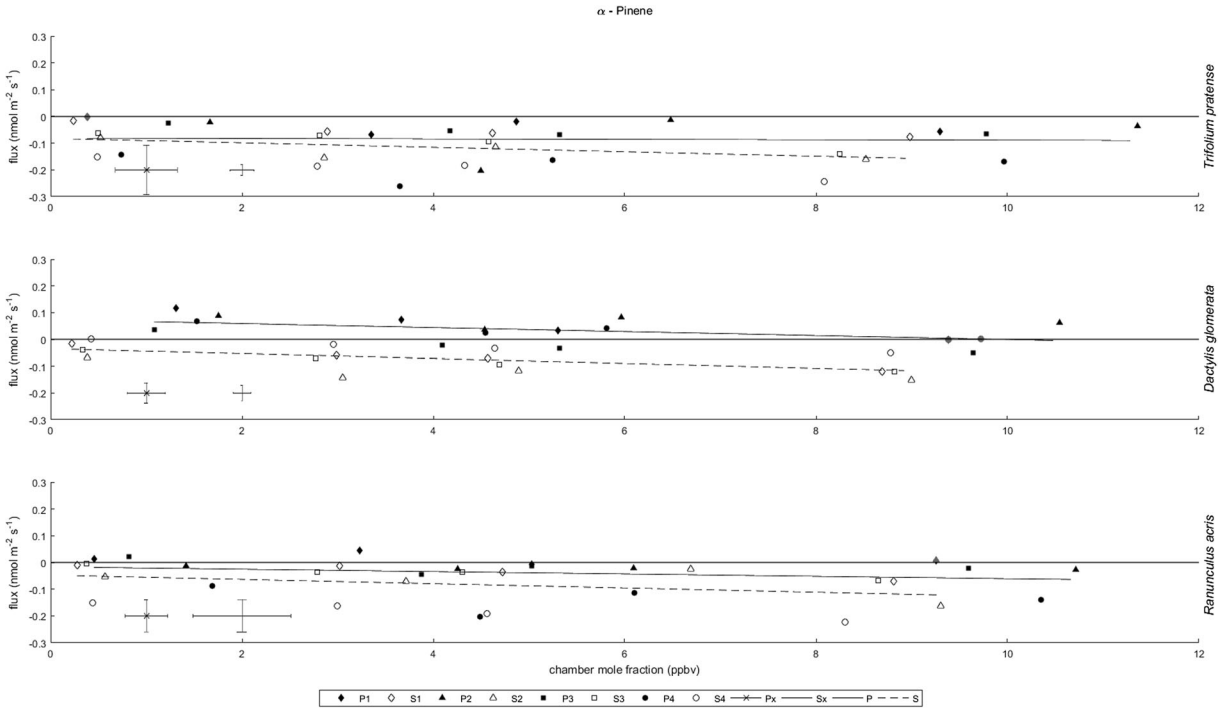

Fig. 3 α-pinene exchange of *Ranunculus acris* (lower panel), *Dactylis glomerata* (middle panel) and *Trifolium pratense* (upper panel) as a function of the ambient α-pinene mole fraction. Negative fluxes denote deposition, positive fluxes the reverse. Open symbols and dashed lines indicate pots with bare soils (S), while closed symbols and solid lines indicate pots with above-ground plant biomass (P) being present. For each plant species four replicate pots were investigated (n = 4). Each data point represents the average of 15 min of measurements at the same ambient mole fraction; the maximum standard deviations per measurement cycle (over the course of all BVOC ambient concentrations) are indicated in the lower left corner of each panel. Grey symbols indicate fluxes below the limit of detection, which were excluded from the statistical analysis

comparison to the 0–10 ppbv used in this study. Nonetheless, Pegoraro et al. (2006) observed a similar pattern of higher isoprene deposition to the soil of tropical rainforests with increasing ambient isoprene concentration. Isoprene deposition was inferred to occur in the lower part of forest canopies also by Karl et al. (2004) and Gordon et al. (2014). In the study of Aaltonen et al. (2012) isoprene deposition was determined to occur regularly to a boreal forest floor during nighttime, although the authors stated that negative fluxes during nighttime coincided with periods of high air humidity inside their chambers and could thus be caused by deposition to the moist surface of the chambers. The isoprene exchange per unit soil surface area determined by Aaltonen et al. (2012) (−2.2 to 5.2 ng m^{-2} s^{-1}) was in the same range as the isoprene fluxes obtained in our study (−41.9 to 2.1 ng m^{-2} s^{-1} and −53.1 to 7.9 ng m^{-2} s^{-1}) for pots including and excluding above-ground biomass, respectively.

In addition to the bi-directional exchange of isoprene, Aaltonen et al. (2012) were also able to quantify monoterpene fluxes to the forest floor in the range of −13 to 260 ng m^{-2} s^{-1}, which are one order of magnitude higher than the fluxes obtained in our study which cover a range of −39.7 to 24.2 ng m^{-2} s^{-1}. The differences in emission can be ascribed on one hand to the plant species composition (coniferous vs. grassland species), since none of the plant species used in our experiment is known to emit monoterpenes in significant amounts. The other difference compared to the experiments of Aaltonen et al. (2012) is that with our experimental setup measurements of m/z 137.133 amu (protonated $C_{10}H_{16}$) can be assigned almost entirely to α-pinene (except for unknown, but likely very low emissions of other monoterpenes), while Aaltonen et al. (2012) quantified the sum of monoterpenes at m/z 137. Noe et al. (2008) were able to quantify deposition fluxes of the monoterpene limonene (0.9–6.0 nmol m^{-2} s^{-1} leaf area) in an experiment with 13 different plant species at saturated partial pressures. Since the α-pinene ambient concentrations used in the present study remained well below saturation, the maximum deposition rates per unit

leaf area measured herein were also by a factor of 10 lower.

Bamberger et al. (2011) observed monoterpene deposition to a managed mountain grassland from which the plants of our experiment originated. The peak deposition values under these natural conditions ranged between 3.3 and 3.9 nmol m^{-2} s^{-1} on a green area and 22 nmol m^{-2} s^{-1} on a ground area basis. Bamberger et al. (2011) also observed that the deposition flux increased with higher ambient monoterpene concentrations (up to 7.5 ppbv). In comparison to these field observations, the deposition fluxes of α-pinene to pots including the above-ground biomass in the present study just reached values up to 0.63 nmol m^{-2} s^{-1} on a leaf area basis. This difference in VOC uptake may originate from the fact that our measurements reflect a single compound, α-pinene, only, while Bamberger et al. (2011) quantified the sum of monoterpenes. In addition, the total amount of leaf area, plant species composition (beyond the three species used in this study) and soils were not as complex in our experiment and may thus account for the differences to the study of Bamberger et al. (2011). The maximum monoterpene uptake rate (0.004 nmol m^{-2} s^{-1} on a soil area basis) published by Asensio et al. (2007) of the VOC exchange rate for a Mediterranean soil, where α-pinene was identified as one of the most important compounds, was similar to the α-pinene-uptake observed for the lowest ambient concentrations in our study (Fig. 3).

An alternative mechanism for the dry deposition of isoprene has been proposed by Enami et al. (2012a) and Enami et al. (2012b). The authors suggest that isoprene deposition to mildly acidic environmental surfaces could be significantly stronger than the uptake by physical condensation or dissolution in the bulk aqueous phase. Although the soil pH we measured was slightly acidic, it was much less acidic than the surfaces tested by Enami et al. (2012b), which had a pH below 5. In a second study by Enami et al. (2012a), the authors suggested that a "significant uptake of gaseous terpenes is expected to take place on the surface of leaves or soils that are that are only mildly acidic" and below a pH of 4. Since the pH is logarithmically scaled, this represents a substantial difference in acidity compared to our soils, which could decrease the impact of this mechanism. Although we didn't measure the leaf-surface pH, we observed that the plants didn't contribute significantly to the uptake of isoprene as well as α-pinene (Figs. 2 and 3). This may however be different under in situ field conditions, due to the potential deposition of acidic particles onto leaf surfaces.

In our second hypothesis (H2) we assumed that even so-called non-emitting plant species would exhibit some residual isoprene and α-pinene emission and that the net effect of this residual emission would reduce the overall deposition compared to pots with soils only. We cannot reject this hypothesis, as the net deposition to soils exceeded the one to mesocoms including above-ground vegetation or they showed less emission in 89 and 83 % of all cases above the limit of detection for isoprene and α-pinene, respectively (Figs. 2 and 3). This indicates that even plants not known to emit significant amounts of certain VOCs, might contain these compounds or their precursor substances, which could explain that in most cases the deposition was lower to pots including above-ground biomass. Findings along this line have been reported by Brilli et al. (2011), who were able to quantify fragments of methylbutanals or pentenols (and isoprene) emission from wounded leaves of *Dactylis glomerata*.

Conclusion

In conclusion, with this study we show that (i) soils were the major sink for the deposition of α-pinene and isoprene in mountain grassland mesocosms, (ii) the presence of above-ground biomass of so-called non-emitting plant species decreased the isoprene and α-pinene deposition, and (iii) the net deposition correlated inversely with the corresponding ambient concentrations. Our results call for a more in-depth analysis of soil biogenic VOC exchange to better estimate the contribution of soils to the ecosystem-atmosphere BVOC exchange in order to allow for the representation of this component flux in biogenic VOC emission models (Guenther et al. 2012).

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